University of Dundee

Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration-flow relationships

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Characterising phosphorus and nitrate inputs to a rural river using high-frequency concentration-flow relationships

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Abstract

The total reactive phosphorus (TRP) and nitrate concentrations of the River Enborne, southern England, were monitored at hourly interval between January 2010 and December 2011. The relationships between these high-frequency nutrient concentration signals and flow were used to infer changes in nutrient source and dynamics through the annual cycle and each individual storm event, by studying hysteresis patterns. TRP concentrations exhibited strong dilution patterns with increasing flow, and predominantly clockwise hysteresis through storm events. Despite the Enborne catchment being relatively rural for southern England, TRP inputs were dominated by constant, non-rain-related inputs from sewage treatment works (STW) for the majority of the year, producing the highest phosphorus concentrations through the spring-summer growing season. At higher river flows, the majority of the TRP load was derived from within-channel remobilisation of phosphorus from the bed sediment, much of which was also derived from STW inputs. Therefore, future phosphorus mitigation measures should focus on STW improvements. Agricultural diffuse TRP inputs were only evident during storms in the May of each year, probably relating to manure application to land. The nitrate concentration-flow relationship produced a series of dilution curves, indicating major inputs from groundwater and to a lesser extent STW. Significant diffuse agricultural inputs with anticlockwise hysteresis trajectories were observed during the first major storms of the winter period. The simultaneous investigation of high-frequency time series data, concentration-flow relationships and hysteresis behaviour through multiple storms for both phosphorus and nitrate offers a simple and innovative approach for providing new insights into nutrient sources and dynamics.

Key words

Point source, Diffuse source, Hysteresis, Nutrient dynamics, Eutrophication, Source tracking.

1 Introduction

Reducing the concentrations of the major plant nutrients, phosphorus (P) and nitrogen (N), is often considered the principal means of delivering improved ecological status of rivers. It is a key requirement for complying with national and international environmental legislation, such as the European Union's Water Framework Directive (CEC., 2000) and nutrient criteria in the USA (Evans-White et al., 2013). Accurate apportionment of P and N inputs from sewage treatment works (STW) and from agricultural and other diffuse catchment sources is a vital component in combating the eutrophication of rivers, estuaries and coastal waters in a cost-effective manner (Withers et al., 2009). Characterising these nutrient source inputs is complex, given seasonal variations in the hydrological stores and pathways, and the superimposed storm event responses. The effects that these changing source inputs have on river nutrient concentrations are further complicated by complex and rapid within-river nutrient dynamics and chemical and biological retention/release processes (Bowes and House, 2001; Jarvie et al., 2012) and these also need to be understood to allow effective catchment management (Jarvie et al., 2013).

Water quality time series data provide a principal means of investigating river nutrient source dynamics. Many chemical and physical parameters, such as pH, dissolved oxygen, turbidity and river flow, have been widely available at near-continuous monitoring interval for many decades, owing to the availability of *in situ* probes. However, nutrient concentration data have traditionally relied on laboratory assays and relatively low temporal resolutions; typically with monthly or at best weekly sampling interval, or daily or storm event data for short durations. Sampling at low (weekly or longer) frequency fails to capture many of the complex and potentially rapid changes in river nutrient signals linked to hydrological and in-stream biogeochemical drivers (Bowes et al., 2009b; Halliday et al., 2012; Kirchner et al., 2004), and often results in large errors in load estimations due to missing intermittent high or low nutrient concentrations during storm events (Bowes et al., 2009b; Johnes, 2007; Rozemeijer et al., 2010). Over the last decade, technological advances in auto-analyser and probe design have allowed high-frequency long-term nutrient concentration data to be produced for the first time, giving new insights into riverine P and N dynamics and sources (Bieroza et al., 2014; Bowes et al., 2012b; Gkritzalis-Papadopoulos et al., 2012; Jordan et al., 2007; Palmer-Felgate et al., 2008; Rozemeijer et al., 2010; Wade et al., 2012). This monitoring has revealed the presence of diurnal nutrient cycling, and rapid concentration changes through individual storm events (Bowes et al., 2012b; Jordan et al., 2005; Palmer-Felgate et al., 2008; Wade et al., 2012).

The coupling of nutrient concentration and river flow data has been successfully used in recent years to develop two separate approaches for inferring nutrient source inputs: nutrient concentration-flow relationships and hysteresis studies. Although the input data is the same (paired nutrient concentration and flow data), the two approaches are subtly different. Nutrient concentration–flow relationships (usually at weekly temporal resolution) have been used in previous studies to infer the relative nutrient contributions to the river from constant and rain-related inputs (Bowes et al., 2014), using the Load Apportionment Modelling approach (Bowes et al., 2008; Bowes et al., 2009a; Chen et al., 2013; Greene et al., 2011; Jarvie et al., 2012; Jarvie et al., 2010). A river dominated by constant nutrient inputs (largely equivalent to STW effluent inputs in the UK) will form a dilution curve with negative gradient as flow increases. Conversely, a river dominated by rain-related inputs (equating to agricultural and septic tank inputs and within-channel mobilisation) will have an increasing nutrient load and/or concentration with increasing flow (Jordan et al., 2007; Wood et al., 2005). Therefore, these fundamental differences in the concentration-flow relationship can be used to infer nutrient source inputs. To date, nutrient concentration-flow relationship studies have largely been limited to applications with weekly nutrient data, which is only capable of providing information on seasonal inputs. High-frequency nutrient concentration and flow data also allow hysteresis effects during individual storm events to be observed. Hysteresis studies examine the differences in nutrient concentrations on the rising and falling limb of the storm hydrograph. If nutrient concentrations are greater on the rising limb, this produces a clockwise loop in the concentration / flow relationship, indicating that the nutrient load is being transported rapidly to the monitoring point. Conversely, anticlockwise loops are produced when highest nutrient concentrations are observed on the falling limb of the storm hydrograph, indicating a slower delivery to the river monitoring point. This approach has yielded valuable information on potential nutrient source inputs to the river, based on how fast the nutrients are delivered in response to rainfall, and whether sources are adjacent to or distant from the monitoring site (Bowes et al., 2005a; Bowes et al., 2009b; Ide et al., 2008; Stutter et al., 2008).

The aim of this study was to generate high-frequency nutrient concentration and flow data to investigate the changing sources of P and nitrate (NO_3) to the River Enborne in response to short-term weather-induced variations throughout a two year monitoring period. This data set has been examined in previous studies, which have highlighted the complex nature of the nutrient signals in response to changes in flow, and the presence of diurnal nutrient cycles at low flows (Halliday et al., 2014; Wade et al., 2012). The aim of this paper is to increase our understanding of these complexities by the simultaneous application of three data interpretation methodologies; analysis of traditional high-frequency time series data, concentration-flow relationships and hysteresis behaviour through all storm events for both phosphorus and nitrate. The simultaneous application of these three methodologies to this high-frequency data set provides a novel approach to providing new insights into the sources and timings of nutrient inputs at different temporal resolutions: annually, seasonally, monthly and during individual storm events.

1.1 Study area

The River Enborne is a small tributary of the River Kennet; a major tributary of the River Thames in southern England (Figure 1). The River Enborne has a catchment area of 148 km^2 and a total length of approximately 30 km. Most of the rivers of the western Thames basin region are groundwater–dominated Chalk rivers, but much of the Enborne catchment is underlain by a layer of low permeability Tertiary clays (Evans and Johnes, 2004), which means that the river is much more hydrologically responsive to rainfall, with a base flow index of 0.54 (Marsh and Hannaford, 2008). The Enborne catchment is relatively rural, being mainly comprised of arable (39 %) improved grassland (27 %) and woodland (23%). Only 6.5 % of the land cover is designated as urban or semi-urban development (Fuller et al., 2002), which is mainly around the outskirts of Newbury and the town of Kingsclere. The total population within the catchment was approximately 18,000 people, with a density of 123 people km^{-2}. This was much lower than the average of 450 people km^{-2} in southern England (excluding London) (Halliday et al., 2014) and the 960 people km^{-2} in the entire Thames basin (Merrett, 2007). There are five STWs in the catchment, with a total population equivalent (PE) of 11360. The largest STW serve the villages around the Wash Common area (PE = 7000), Kingsclere (PE = 2500) and Greenham Common (PE = 1700) (Halliday et al., 2014). The mean annual rainfall and river flow at Brimpton for the period 1967 to 1995 is 810 mm and 1.33 m^3 s^{-1} respectively (Marsh and Hannaford, 2008). The high-frequency water quality monitoring station was sited near the village of Brimpton (British National Grid: SU569649) in the lower part of the catchment, a few km from the confluence with the River Kennet at the village of Aldermaston (Figure 1). The monitoring station was established as part of the LIMPIDS project (Wade et al., 2012). River flow data at 15 minute resolution was measured at the adjacent Environment Agency flow gauging station, and data was supplied through the Centre for Ecology’s National River Flow Archive. More detailed descriptions of the River Enborne catchment are given elsewhere (Evans and Johnes, 2004; Halliday et al., 2014; Wade et al., 2012).

2 Methods

2.1 Chemical analysis

2.1.1 High-frequency automated nutrient analysis

High frequency monitoring was carried out within a heated and insulated monitoring station adjacent to the River Enborne near Brimpton (Figure 1). The data used in this study were gathered between January 2010 and December 2011. A detailed description of the monitoring facility and instruments are given elsewhere (Halliday et al., 2014; Wade et al., 2012), and so only a brief overview will be presented here. *In situ* hourly P analysis was carried out using a Systea Micromac C autosampler / analyser (Systea S.P.A., Anagni, Italy). This instrument measured the total reactive phosphorus (TRP) concentrations of an unfiltered river water sample, using the molybdate-blue colorimetric methodology of Murphy and Riley (1962). To avoid problems of instrument drift the instrument auto-calibrated once per day using a certified quality control standard. The limit of detection (LOD) was 25 µg P L^{-1}. NO_3 concentration was measured at hourly interval by ultraviolet absorption using a Nitratax Plus probe (Hach Lange GmbH, Düsseldorf, Germany) (LOD = 0.07 mg N / L^{-1}). The NO_3 and TRP data were validated against laboratory-based analytical data from weekly manual samples. A full statistical assessment of the quality of the high-frequency data compared against the traditional laboratory data is given in Halliday et al. (2014).

2.1.2 Laboratory analysis of manual samples

Water samples were taken from the main flow of the River Enborne at Brimpton at weekly intervals throughout the two year monitoring period, as part of the Centre for Ecology and Hydrology's Thames Initiative research platform (Bowes et al., 2012a). These data were used to investigate P and

N speciation in the River Enborne and also to validate the automated high-frequency data sets. Soluble reactive phosphorus (SRP) and TRP were determined spectrophotometrically by the phosphomolybdenum-blue complexation of a filtered and unfiltered water sample respectively (Murphy and Riley, 1962). Total phosphorus (TP) and total dissolved phosphorus (TDP) concentrations were determined by acid-persulphate digestion of unfiltered and filtered water samples respectively, followed by complexation using acidified ammonium molybdate (Eisenreich et al., 1975). NO_3 and nitrite concentrations were determined by ion chromatography (Dionex DX500). Ammonium and dissolved reactive silicon (Si) concentrations were also determined by spectrophotometry, using the methods of Krom (1980) and Mullin and Riley (1955). Total dissolved nitrogen (TDN) and dissolved organic carbon concentrations were determined by thermal oxidation. All samples were run alongside external quality control standards (LGC, Bury, UK). Full details of the analytical methods used in this study are given in Neal et al. (2012).

2.2 Characterisation of hysteresis trajectories

There were 36 distinct storm events identified from the River Enborne hydrograph throughout the two-year monitoring period (Figure 2). Through the high flow months (December to April) within the monitoring period, all events resulting in a > 60% increase in flow were selected. During the low flow periods (May to November), events resulting in a > 40% increase in flow were selected, as these events were preceded by long periods of dry weather, and therefore more likely to make important contributions to nutrient inputs. The TRP and NO_3 concentrations through each of these storm events were investigated for the presence of hysteresis patterns. Hystereses in the concentration-flow relationships are often observed during storm events, i.e. the concentration of a determinand, at a given river flow, is different on the rising and falling limb of a hydrograph (Hall, 1970). When plotted, such concentration/flow relationships result in ‘‘loop trajectories’’, with a clockwise hysteresis loop produced when the concentration is higher on the rising limb of the hydrograph, and an anticlockwise loop when the concentration is higher on the falling limb. The high-frequency TRP and NO_3 concentration data were plotted against river flow for each of the individual storm events, to determine the direction of the hysteresis trajectory (clockwise, anticlockwise, no hysteresis or a more complex pattern). The size of the loop trajectories were quantified by determining the difference in concentration on the rising and falling limbs of the hydrograph, at the midpoint river discharge of the storm peak (Lawler et al., 2006).

3 Results and Discussion

3.1 Nutrient concentrations

3.1.1 Phosphorus

The high-frequency TRP concentration data for the River Enborne at Brimpton are presented in Figure 2(a), with accompanying rainfall and river flow data. The average TRP concentration throughout the two year monitoring period was 178 µg P l^{-1} (based on 13343 observations) (Table 1), which means that the River Enborne is classified as eutrophic (Dodds et al., 1998). Similar mean SRP concentrations for the River Enborne were observed at the Brimpton study site between 1998 to 2000 (Evans and Johnes, 2004), indicating that there has been no improvements in water quality over this time. Weekly water quality monitoring data throughout 2010 and 2011 demonstrated that 67% of the TP load was in a soluble reactive form (Table 1). Mean TRP concentrations were on average 17% higher than SRP concentrations, indicating the presence of a significant particulate-bound reactive P fraction in the River Enborne.

TRP concentrations followed a clear annual cycle throughout the monitoring period (Figure 2), with lowest TRP concentrations through the January to May period, followed by a steady increase from May to August. The highest TRP concentrations of approximately 590 µg l^{-1} occurred during August and October 2010, at times of very low flow (<0.25 m^3 s^{-1}). The lowest TRP concentrations of <10 µg l^{-1} occurred in early March 2010, and are likely to be due to biological uptake at the onset of the spring diatom bloom that occurred in many rivers across the Thames basin at that time, as indicated by increases in chlorophyll concentration and decreases in dissolved reactive silicon concentrations

(Bowes et al., 2012a). Weekly water quality monitoring data from the River Enborne at Brimpton showed reductions in dissolved reactive silicon concentrations of approximately 3.5 mg Si l^{-1} during March 2010 and 2011, compared to concentrations of approximately 8 mg Si l^{-1} during the winter months. This seasonal pattern appears to be principally driven by the hydrology, with high TRP concentrations coinciding with low flow periods in summer and autumn, and low TRP concentrations during the high flow winter and spring periods, indicative of dilution of dominant point sources. For the River Enborne, these point sources will mainly consist of STW inputs (Halliday et al., 2014)The impact of hydrology is further confirmed by the sudden short-term reductions in TRP concentration that coincide with short periods of rainfall during the summer periods, as shown during storm peaks 16, 18 and 19 in 2010 and peaks 29 and 30 in 2011 (Figure 2(d)). Conversely, some of the smaller storm events (peaks 13, 14, 21 and 33) caused sudden increases in TRP concentration. This demonstrates the complex nature of phosphorus dynamics that are operating within this catchment, which can only be observed and investigated when high temporal resolution data are available.

3.1.2 Nitrogen

The total dissolved nitrogen (TDN) load of the River Enborne was predominantly present in the form of nitrate (90 %), with nitrite and ammonium contributing only 0.5 % and 1.3 % of the average TDN load respectively, based on the weekly water quality data (Table 1). The high-frequency NO_3 concentrations throughout the monitoring period were less variable than TRP, ranging from maximum concentrations of 6.24 mg N l^{-1} NO_3–N through the late spring and summer periods, and falling to between 2 and 4 mg N l^{-1} in the winter months, with an average concentration of 4.0 mg N L^{-1} (from a total of 15752 data points). Again, there is a clear hydrological effect, with sudden reductions in NO_3 concentration coinciding with periods of intensive rainfall, particularly during storm 16, 19, 29, 30 and 33 (Figure 2(d)). There was close agreement between the high-frequency nitrate data and the nitrate concentrations of the accompanying weekly manual samples analysed by standard laboratory assays (Figure 2(b)), showing that the Hach Lange Nitratax probe was producing high quality, accurate data throughout the monitoring period. A full statistical assessment of the quality of this data against the traditional laboratory analysis is given in Halliday et al. (2014).

3.2 Nutrient concentration-flow relationships

3.2.1 Total reactive phosphorus

The TRP concentrations in the River Enborne throughout the two year monitoring period demonstrated a clear relationship with flow (Figure 3(a)). Highest TRP concentrations occurred at low flows, with all concentrations greater than 300 μg P l^{-1} occurring at flows less than 2.1 m^3 s^{-1}. These high TRP concentrations decreased rapidly with increasing flows, producing a dilution curve. The lowest TRP concentrations occurred at flows ranging from 2 to 3.5 m^3 s^{-1}. These data points coincide with high chlorophyll concentrations and low silicon concentrations, indicating they were due to biological uptake by biofilms. At flows above 2.5 m^3 s^{-1}, TRP concentrations were consistently between 30 and 100 μg P l^{-1}. Similar P concentration-flow relationships were observed in the River Enborne in the late 1990s (Evans and Johnes, 2004), and at multiple sites along the River Thames and many of its tributaries since 2009 (Bowes et al., 2014). These relationships are indicative of mixed urban / rural catchments with dominant point source inputs from STW (Bowes et al., 2010; Bowes et al., 2008; Bowes et al., 2009a; Jarvie et al., 2006; Jordan et al., 2007).

The vast majority of TRP data points conformed to this well defined pattern with flow. However, there were some data points at higher than expected TRP concentrations for a given river flow. Many of these (at flows less than 2.5 m^3 s^{-1}) are probably either due to analytical noise and short term errors with the Systea TRP analyser or flow gauging data, or possibly due to localized, short term pollution incidents that were not related to rainfall (Jordan et al., 2005). At flows greater than 2.5 m^3 s^{-1}, these higher, "non-conforming" TRP concentrations were all associated with hysteresis patterns during storm events (Figure 3(a)). The largest deviations from the standard TRP / flow pattern occurred during flow peaks 16, 19, 22 and 26 (Figure 2(d)), which were all storm events following long periods of dry antecedent conditions, indicating that there had been a build up of a transportable TRP supply within the catchment during these dry periods, followed by flushing during the subsequent storms.

3.2.2 Nitrate

The relationship between NO_3-N concentration and flow was more complex than that of TRP. Again, the highest concentrations occurred at the lowest flows, with almost all NO_3–N concentrations greater than 5 mg N l^{-1} occurring at flows less than 1 m^3 s^{-1} (Figure 3b). There was a pronounced series of dilution curves with increasing flow, reducing the NO_3 concentration to below 3 mg N l^{-1} as flow increased to above approximately 4 m^3 s^{-1}. Some of these dilution curves were directly related to individual large storm events (peaks 1 and 8; Figure 2d). These reductions in NO_3 concentration with increasing flow suggest that rainfall events were diluting a relatively constant input of NO_3. The rate of dilution was much less than for TRP concentration, and produced a series of curves, rather than the single dilution curve observed in the TRP concentration/flow relationship. These observations suggest that there are multiple sources of NO_3 that are being diluted by storm events, some of which are constant (e.g. STW inputs) and others that continually supply NO_3 through the annual cycle, but at a rate that varies with river flow and rainfall (e.g. groundwater inputs) (Halliday et al., 2014). The relationship is further complicated by varying rates of diffuse inputs and exhaustion of catchment supply through different storm events at different times of the year.

Another characteristic of the NO_3 concentration-flow relationship for the River Enborne was the cluster of low NO_3 concentrations (< 3 mg N l^{-1}) at very low river flow (< 1 m^3 s^{-1}) (Figure 3(b)). These data points occurred throughout the annual cycle, and so are unlikely to be due principally to within-stream biological processes such as bioaccumulation and denitrification. This data cluster was almost entirely comprised of data points that occurred during small storm peaks during low flow periods (storm peaks 16, 21, 29, 31, 32 and 33; Figure 2d), and following dry antecedent conditions. This suggests that the rainfall associated with these small flow peaks was sufficient to dilute the NO_3 concentration in the river (potentially from low-NO_3 concentration sources such as direct precipitation to the river and run-off from roads and paved areas) , without mobilising and transporting the nitrate stores within the catchment. This is probably related to the dry soil conditions preceding these storms minimising rates of overland flow and through-flow as the catchment begins to wet-up, and this will thereby minimise diffuse nitrate inputs. This is further supported by the lack of river flow response following some of the most intensive rainfall events observed through the monitoring period, particularly associated with storm peaks 16, 29 and 31.

In contrast, there were four major hysteresis loops that did not conform to the regular dilution patterns observed through the majority of the annual cycle. These hysteresis loops occurred during some of the largest storm events observed throughout the monitoring period (peaks 1, 22, 24 and 34; Figures 2a and 3b). This indicates that it is only these major storm events that were able to mobilise and transport significant quantities of catchment-stored diffuse nitrate to the river, relative to the STW inputs.

3.3 Seasonal and monthly changes in nutrient sources

3.3.1 Total reactive phosphorus

The seasonal patterns in the TRP concentration-river flow relationship are given in Figure S.1. The large quantity of data generated by the hourly monitoring frequency also allowed TRP concentration / flow relationships to be investigated at monthly resolution (Figure 4). During the summer periods (June to August 2010 and 2011), constant non-flow-related inputs dominated the TRP load, with over 98% of all data points following a clear dilution curve pattern (Figure S.1). STW P inputs were therefore clearly dominant throughout this summer period. When river flows increased above 0.7 m^3 s^{-1} in August 2010 and 2011 (Figure 4), the TRP concentrations deviated from this dilution curve, indicating the input of rain-related P, potentially from diffuse catchment sources and within-channel P remobilisation in response to minor storm events. However, these data represented less than 2% of the total observations throughout this period, producing a maximum concentration of 350 µg TRP l^{-1}, compared to a maximum of 577 µg TRP l^{-1} during the periods of lowest flow.

The rainfall-related diffuse signal increased through the autumn (Figure 4; Figure S.1), in response to the increasing magnitude of the flow peaks that occurred in October and November 2010 and November 2011 (Figure 4). However, the majority of the data points were still on the dilution curve, indicating a continued dominance from constant source STW inputs for the majority of the time. During the winter and spring periods, diffuse TRP sources began to dominate the inputs to the river. During the winter periods, TRP concentration changed little as flows increased above approximately 1.5 $m^3 s^{-1}$, remaining between 30 and 110 µg P l^{-1} (particularly in January and February 2010 and January 2011; Figure 4). This suggests that the additional water entering the river during these storm events (through through-flow and overland flow) was a similar TRP concentration to that in the river, due to it mobilising diffuse phosphorus sources from the catchment. Also, the input of low-P-concentration rainwater would reduce the soluble P concentration in the river, and this could promote the release of particulate-bound P from the bed-sediment into the overlying water column (Bowes and House, 2001; House, 2003). The shift in this sediment–water equilibrium would explain why TRP concentrations are relatively constant with increasing flow during this period.

During the spring period, (particularly March and April 2010), the TRP concentrations again remained relatively constant, irrespective of flow (Figure S.1; Figure 4), indicating diffuse source inputs from the catchment and within-channel remobilisation. The variation in TRP concentration in spring was higher than observed during the winter period, due to some significant storm events causing increases in TRP concentration, and a short-term decrease in TRP concentration due to biological uptake during a diatom bloom (with dissolved reactive silicon concentrations falling by 25% (Bowes et al., 2012a)), both of which occurred in March 2010 (Figure 4). However, even during the winter and spring periods, all of the highest observed TRP concentrations (>300 µg P l^{-1}) occurred at low river flows (less than 1.2 $m^3 s^{-1}$), and clear dilution curves were produced. This indicated that constant, non-rain-related input of TRP were still an extremely important source to the river, and the most likely source of these constant inputs in the Enborne catchment will be from STW effluent.

In a previous study, Load Apportionment Modelling of weekly total phosphorus concentrations at Brimpton estimated that 68% of the P load in the River Enborne came from rain-related diffuse sources (Bowes et al., In press). However, the seasonal and monthly TRP patterns clearly show that, even in this predominantly rural catchment with relatively low population density for southern England, there is a major dominance of constant STW P inputs at low flows, particularly through the ecologically-sensitive late spring to early autumn period (Figure 4) when the risk of algal blooms is at its greatest (Jarvie et al., 2006). In the winter to early spring period, there is an increase in rain-related diffuse inputs, but there continues to be a clear point source signal, and the highest TRP concentrations still occur at the lowest flows at all times of the year. Introducing improved P removal at STW within the catchment would therefore be the most effective way of improving water quality and ecological status of the River Enborne, as it would reduce peak TRP concentrations during the growing period. These monthly TRP concentration-flow relationships highlight that P source inputs are controlled primarily by rainfall and river flow, rather than changes in land use (e.g. crop type, vegetation cover) and management (e.g. manure and fertiliser application) through the annual cycle.

3.3.2 Nitrate

NO_3 concentrations during the winter months remained relatively constant in response to increasing river flows (Figure 4, Figure S.2). The data clearly formed a series of distinct trajectories for individual storm events. Some storms resulted in an increase in concentration with increasing flow (January and December 2011; Figure 4) indicating that the storm water was mobilising significant diffuse N load from the catchment, potentially via through-flow or overland flow. This diffuse storm water input must have had a higher NO_3 concentration than the river water prior to the storm. This large quantity of NO_3 input to the river probably related to the dry antecedent conditions that existed prior to these particular storm events, allowing significant quantities of N to accumulate within the floodplain. The other winter storm events produced trajectories that remained at relatively constant NO_3 concentrations through each particular storm (January 2010; Figure 4), indicating that the diffuse input must be approximately the same concentration as the river water of the River Enborne at the time (approximately 3 mg N l^{-1}). In the subsequent months to April 2010, the NO_3 concentration-flow relationships became progressively more negative in gradient, indicating that diffuse sources of catchment N were probably becoming depleted through the winter to spring period (Figure 4; Figure S.2). From the late spring to early autumn of both years, there were no significant flow peaks, and the NO_3 concentrations consistently formed dilution curves for each month, indicating a dominance of constant inputs (Figure 4). For the River Enborne, these constant NO_3 sources equate to both STW effluent inputs and groundwater sources. In October and November 2010, and August and November 2011, small flow peaks caused a marked increase in river NO_3 concentration with increasing flow, again indicating the mobilising of the large store of NO_3 that had accumulated across the catchment through the dry antecedent conditions.

The highest NO_3 concentrations occurred between April and October of each year, during low flow periods, indicating a dominance of constant, non-rain-related inputs. Some of the lowest concentrations also occurred during these low-flow periods. Almost all of these low concentration data points were associated with minor storm events (Peaks 16, 21, 29, 31, 32 and 33; Figures 2 and 3), which implies that these events dilute the NO_3 load in the river without mobilising any substantial diffuse NO_3 inputs from the catchment, and it is this rainwater input that is diluting the NO_3 concentration in the river.

3.4 Changes in nutrient concentrations through individual storm events

The nutrient concentration-flow hysteresis patterns through all 36 storms are given in Table 2 and Figure 5, with an example of typical TRP and NO_3 hysteresis trajectories given in Figure S.3.

3.4.1 Total reactive phosphorus hystereses

TRP concentrations produced clockwise hystereses for 21 of the 30 storm peaks that had accompanying P data (i.e. TRP concentration was greater on the rising limb of the hydrograph than at the same flow on the falling limb of the hydrograph). Previous studies of lowland UK rivers have also observed a general predominance of clockwise P hysteresis (Bowes et al., 2005a; House and Warwick, 1998; Jordan et al., 2005; Stutter et al., 2008). Most of the largest storm events tended to produce clockwise trajectories, but the largest clockwise loop trajectories usually occurred following periods of relatively dry conditions (August 2010 and January 2011; Figure 5). The predominantly clockwise trajectories indicated that TRP sources in the River Enborne were rapidly mobilised and transported to the monitoring site during storm events. Potential sources would include near-channel stored phosphorus along the river channel margins (in the form of septic tanks, animal faeces, soil/bank erosion and dead organic material) that would be intercepted, entrained and delivered to the channel as water levels rise through a storm event. Field drains would also potentially provide a rapid route of P inputs to the river. Another significant potential source of rapidly mobilised TRP would include phosphorus that had been stored within the bed sediment of the river, and was entrained into the water column as flow velocity increased through the storm event (Bowes and House, 2001; Jarvie et al., 2012). Many of the largest clockwise hysteresis storm events (Peaks 10, 16, 19, 22 and 26; Figure 2) were responsible for producing the scatter in the TRP concentration-flow relationship (Figure 3), suggesting that most of this additional P producing the scatter is due to these rapidly-mobilised P sources.

The series of storm events from December 2010 to March 2011 shows a transition from large clockwise loops during the early storms, to decreasing clockwise loop trajectories in January and February, and by the end of February, the final storm event did not produce a hysteresis pattern. Similar trends through a series of storm events have been observed in previous studies (Bowes et al., 2005a; Stutter et al., 2008), and been attributed to a gradual depletion of these rapidly-mobilised, within-channel and near-channel P sources. Only four anticlockwise TRP hysteresis loops were observed during the two year monitoring period, and were all associated with relatively small storm events with a maximum river flow of < 3 $m^3 s^{-1}$ (Table 2, Figure 5). Anticlockwise trajectories occur when the P load through the storm event is dominated by TRP sources that are slow to reach the monitoring site, implying that these sources may be some distance from the river channel. Potential sources are diffuse agricultural inputs from throughflow and overland flow, derived from the wider catchment. Three of the four anticlockwise hysteresis patterns occurred in May, and could be potentially related to fertiliser and slurry applications that occur during this period across the UK (Figure 6).

3.4.2 Nitrate hystereses

The NO_3 hysteresis patterns were also predominantly clockwise in trajectory, accounting for 21 of the 36 storm events monitored (Table 2; Figure 5). All of these clockwise trajectories were associated with relatively small storm events (with maximum flows ≤ 7.5 $m^3 s^{-1}$). They occurred throughout the annual cycle, but were more common during the summer periods. All nine storm events during the relatively dry May to December 2010 period produced clockwise hysteresis patterns. The largest clockwise hysteresis trajectories occurred between May and November, following long periods of dry antecedent conditions. Clockwise hysteresis indicates a rapid delivery of nitrate to the river in response to rainfall, and in a catchment such as the River Enborne, potential sources of this rapidly-mobilised N could be from mobilisation along river margins and delivery through field drains. However, half of these storms produced hysteresis trajectories with negative gradients, indicating that the storm events were primarily diluting the nitrate concentration in the river.

Only six of the 36 storm events produced anticlockwise NO_3 hysteresis trajectories. These all occurred between November and January, and tended to be associated with large storm events with flows ≥7.5 $m^3 s^{-1}$. Four of the five largest storm events during the monitoring period produced anticlockwise hysteresis patterns. This indicates that slowly-mobilised catchment-wide diffuse sources only become dominant during these large storm events (particularly after the catchment has started to wet-up through the winter period) (Figure 6). This input of large quantities of additional catchment-wide nitrate to the river system creates most of the "non-conforming" data from the nitrate concentration-flow relationship, shown in Figure 3, with peaks 1, 22, 24 and 34 all producing large anticlockwise hysteresis trajectories. Nine of the 36 storm events produced either no hysteresis, or complex, multi-loop trajectories. This suggests that the NO_3 loading to the River Enborne is more complex than for phosphorus, probably due to the significant and complex role that NO_3-rich Chalk groundwater plays (Neal et al., 2002a), in combination with the rapid, lower nitrate concentration surface run-off from the impervious Tertiary clays of the catchment.

3.5 Synthesis of approaches

Generating this high-frequency dataset has allowed nutrient sources to be simultaneously investigated using three different approaches. Firstly, the raw time series data provides background information about seasonality and response to rainfall (Figure 2), which can be directly compared with other time series (such as chlorophyll or dissolved silicon concentration) to identify periods of nutrient depletion due to biological productivity (Figure 6). Secondly, when combined with high-frequency river flow data, the resulting concentration-flow relationship provided information on the relative inputs of nutrient sources, based on whether their delivery is constant or related to rainfall. The vast quantity of data generated in this study has allowed the nutrient concentration-flow relationship to be further investigated at higher temporal resolution, both seasonally (Figure S.1; Figure S.2), and, for the first time, down to a monthly resolution (Figure 4). Thirdly, the hourly chemistry and associated flow data allowed changes in nutrient concentration to be investigated through each individual storm event, and the interpretation of the hysteresis trajectories provided detailed information on the speed of mobilisation and delivery of the nutrient sources to the monitoring site. These three approaches provide subtly different interpretations, and when brought together, can provide new understanding of nutrient sources and catchment management guidance.

3.5.1 Phosphorus sources

TRP concentrations show a clear seasonal pattern. This appears to be driven by rainfall and river flow rather than short term variations in land use, as months with similar flow range produce almost identical concentration-flow relationships, irrespective of the time of year (e.g. August and October 2010; May and December 2010; Figure 4). The presence of clear dilution curves through the seasons shows that constant sources of P dominate for the majority of the annual cycle, producing the highest observed TRP concentrations. The only plausible source of these constant inputs in the River

Enborne is from sewage effluent from its five STW and, to a lesser extent, septic tank discharges direct to the watercourse (Figure 6). Similar conclusions of sewage dominance in the River Enborne have also been deduced from examining the diurnal patterns in TRP concentration (Halliday et al., 2014). Relatively constant TRP inputs from groundwater will be negligible, due to low P concentrations in the Chalk groundwater matrix, resulting from the co-precipitation of P with $CaCO_3$ within the Chalk aquifer (Bowes et al., 2005b; Neal et al., 2002b). However, the annual TRP concentration-flow relationship also showed that a significant proportion of the TRP load was derived from rain-related inputs (Figure 3). This could be from inwash of diffuse agricultural pollution from across the entire catchment, via through-flow, overland flow, shallow groundwater flow, field drains and direct entrainment of nutrients along the river margins, along with septic tank inputs and mobilisation of P from river bed sediment. However, the hysteresis study has shown that storm events produced predominantly clockwise hysteresis throughout the year (Figure 5), which means that the rain-related sources are being rapidly delivered to the monitoring site. This strongly suggests that the majority of the rain-related load can only be derived from sources that are predominantly rapidly transported, such as field drains, river margins and bed-sediment mobilisation, and not via predominantly slower delivery routes such as through-flow, or from distant parts of the catchment.

3.5.2 Nitrate sources

The NO_3 concentration-flow relationship was more complex, consisting of a series of dilution curves (Figure S.2). This indicated a major continual input from constant (STW effluent) and relatively-constant (groundwater) sources. The rate of 'constant' input varied with rainfall, producing this series of dilution curves, which strongly suggests that it is groundwater, rather than STW effluents, providing the major load input to the River Enborne. Similar conclusions have been reached based on mass-balance studies of the River Enborne catchment (Halliday et al., 2014), and many previous studies of Chalk catchments in southern England have shown the high concentrations of nitrate groundwater contamination (Jarvie et al., 2005; Smith et al., 2010). Most of the smaller storm events produced clockwise hysteresis (Table 2, Figure 5), indicating a predominance of rapidly delivered NO_3 sources. Many of these storm events producing hysteresis loops with a very negative gradient (peaks 16, 21, 29, 32 and 33; Figure 3), indicating that the major impact of small storm events during dry periods was actually to dilute the NO_3 concentration, rather than to mobilise and supply large quantities of extra N to the river. The only time that substantial quantities of additional NO_3 (relative to the constant inputs from groundwater and STW) were supplied to the river was during major winter storm events (e.g. peaks 1 and 8; Figure 3). These deductions of potential NO_3 sources are summarised in Figure 6.

3.5.3 "Non-conforming" data points

The TRP concentration-flow relationship for the River Enborne was extremely robust, with the vast quantity of data lying along the dilution curve at low flow, and then levelling out at between 30 and 100 µg P l^{-1} at higher flows (Figure 3). There was also a strong relationship between NO_3 concentration and flow, although it was more complex, due to serial dilution curves (Figure 3, Figure S.2). However, for both TRP and NO_3, there were some scattered data points that had much higher nutrient concentrations than expected, deviating from the usual nutrient concentration-flow relationships. In previous studies based on lower frequency sampling, these "non-conforming" data points would either have been wrongly identified as erroneous observations and rejected from the data set, or would have been interpreted as being due to sporadic pollution incidents (Jordan et al., 2007), and attributed to large scale agricultural diffuse pollution. It has been widely inferred that such events will be greatly underrepresented by traditional monitoring programmes, thereby underestimating the potential impact of agricultural nutrient pollution within catchments. However, combining this concentration-flow approach with hysteresis studies clearly demonstrated that almost all of these data points consist of large hysteresis loops associated with individual storm events, rather than being erroneous data points. The generation of high quality, high frequency datasets are the only way of identifying and quantifying these potentially important nutrient sources.

The "non-conforming" scattered TRP concentration data are exclusively associated with large clockwise hysteresis trajectories, whereas the non-conforming NO_3 concentration data were all associated with large anticlockwise hysteresis (Figure 3). This strongly suggests that these major nutrient inputs are derived from different areas of the catchment. Most of the additional TRP was derived from rapidly mobilised sources and the additional NO_3 was derived from slowly mobilised sources. It is also important to note that these non-conforming TRP and NO_3 hysteresis loops were not produced by the same storm events (with the exception of Peak 22, Figure S.3). This means that the significant quantities of additional TRP load must be largely derived from a rapidly-mobilised source that was not associated with additional NO_3 inputs of a similar magnitude. If they were, the resulting NO_3 hysteresis loop from that storm event would also be represented in the 'non-conforming' data in the NO_3 concentration-flow relationship. This shows that the additional TRP loading could only be derived from the remobilisation of within-channel phosphorus stored within the bed-sediment, as remobilisation of P along the river margins and inputs from septic tanks and field drains would be expected to also have significant NO_3 inputs associated with them. This deduction was further confirmed when the timing of these major non-conforming loops was taken into account. They almost always occurred following a proceeding dry spell, implying that phosphorus is being accumulated within the bed sediment until it is remobilised during the next storm event. During these antecedent dry periods, diffuse agricultural P inputs will be at a minimum, and so the most significant source of P input to the River Enborne will be from STW effluent. Therefore, the majority of the rain-related "diffuse" signal observed in these non-conforming TRP concentration data will actually originate from sewage effluent point sources (Figure 6).

In contrast, the non-conforming NO_3 inputs were exclusively associated with large anticlockwise hysteresis trajectories, and so the major NO_3 source was primarily delivered during the falling limb of the storm hydrograph. As these particular storm events produced major non-conforming NO_3 hysteresis loops, and the associated TRP loops were clockwise and didn't deviate significantly from the standard TRP concentration-flow relationship, the source supplying the additional NO_3 could not be a significant source of P. This discounts major overland flow and delivery via farm tracks, tractor wheel tracks and other rapid pathways as the source, as these would also be associated with major sediment mobilisation, with its large quantities of associated P. All of the non-conforming NO_3 hysteresis loops occurred in December and January, and were associated with some of the largest storm events within the monitoring period. This suggests that the source of this additional NO_3 was either a catchment-wide agricultural N input distant from the river channel, via through-flow (rather than via field drains, as this would also deliver phosphorus), or from slowly-responding groundwater inputs, as these would not contain significant quantities of P, due to precipitation within the Chalk (Figure 6).

Storm event 22 was the only flow peak that produced both TRP and NO_3 non-conforming hysteresis loops (Figure 3, Figure S.3). It was the first large storm event of the 2010 – 2011 winter season, and produced a large clockwise TRP hysteresis trajectory and a large anticlockwise nitrate trajectory. Therefore, although this storm mobilised significant additional P and N, they were derived from different sources, with phosphorus largely derived from rapidly mobilised sources (from within-channel and river margin sources) and the NO_3 mostly derived from slowly-mobilised sources.

4 Conclusions

The monitoring of P and N concentrations at hourly sampling intervals throughout two annual cycles has produced new understanding of the timing and relative quantities of nutrient source inputs to the River Enborne. The combined investigation of P and N time series information, concentration-flow relationships and hysteresis behaviour through individual storm events allowed nutrient sources to be identified through the annual cycle and during specific flow conditions.

- The P inputs to the River Enborne were dominated by STW effluent for the majority of the year, and were responsible for producing the highest TRP concentrations during periods of low flow.
- Increasing river flow through the annual cycle increased the TRP load, but had little effect on TRP concentration, which remained between 30 to 110 µg P l^{-1}. The majority of this rain-related load was derived from within-channel remobilisation of P from the bed sediment, entrainment of P along the river margins and field drain inputs. A number of storm events

produced large clockwise hysteresis patterns that deviated from the usual TRP concentration-flow relationship, and this additional P must be predominantly from bed sediment remobilisation, which would have largely be derived from sewage inputs through the preceding dry periods.

- Future P mitigation of the River Enborne should focus on reducing sewage inputs, as this would reduce TRP concentrations through the ecologically sensitive spring – summer period, and reduce the major hysteresis trajectories associated with bed sediment remobilisation. Diffuse P mitigation should primarily focus on reducing the significant inputs that occur each May, which are probably linked with fertiliser and manure applications and specific land management at that time.
- The NO_3 load of the River Enborne was dominated by constant inputs throughout most the year, primarily derived from groundwater, and to a lesser extent, STW.
- The first major storm events of the winter produced major inputs from catchment-wide diffuse NO_3 sources, probably delivered via throughflow pathways. Diffuse N inputs declined through the subsequent winter and spring storm events, indicating depletion of catchment nitrogen sources.
- Minor storm events during summer produced large inputs of rapidly-mobilised diffuse nitrate (most probably from field drains and river margins), indicating the importance of dry antecedent conditions.

This study has important implications for nutrient studies of other catchments, monitored at the traditional weekly or monthly sampling intervals. Firstly, single data points that can easily be rejected as outliers in low-frequency data sets could often be genuine data points associated with large hysteresis events. Capturing these sporadic hysteresis events can provide fresh insights into nutrient sources and behaviour within the river and its catchment. This study also clearly highlights that nutrient behaviour during storms can vary dramatically through the annual hydrological cycle. This has important ramifications for the many previous studies that focus on a small subset of storm events, and whether these storms are truly representative of all storm events needs to be carefully considered.

High frequency river nutrient data is becoming more widely available and easier to generate, due to recent developments in field autoanalyser / probe technology and telemetry. This study has shown the great utility of these high frequency water quality and flow data sets, and presents a simple, integrated methodology that can be used to disentangle the complex nutrient signals that routinely occur in river systems. Determining nutrient sources and behaviour, at high temporal resolution, provides vital information to allow the most appropriate mitigation options to be selected to combat eutrophication, thereby providing the most effective and cost-effective management of river catchments in the future.

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Tables and Figures

Table 1. Summary of nutrient species concentrations of the River Enborne (January 2010 to December 2011), based on weekly sampling data. Total reactive phosphorus data based on a 14 day sampling interval.

	Soluble reactive phosphorus	Total reactive phosphorus	Total dissolved phosphorus	Total phosphorus	Total dissolved nitrogen	Nitrate	Nitrite	Ammonium		Dissolved reactive silicon	Dissolved organic carbon
	µg P l^{-1}	µg P l^{-1}	µg P l^{-1}	µg P l^{-1}	mg N l^{-1}	mg N l^{-1}	mg N l^{-1}	mg N l^{-1}		mg Si l^{-1}	mg C l^{-1}
Weekly laboratory data											
Mean	138	162	166	206	4.39	4.03	0.020	0.055		7.13	5.4
Maximum	308	352	340	447	6.31	5.68	0.15	0.28		9.90	10.2
Minimum	24	50	65	85	2.40	2.50	0	0		2.96	1.2
High-frequency field data											
Mean	-	178	-	-	-	4.00	-	-	-	-	-
Maximum	-	596	-	-	-	6.24	-	-	-	-	-
Minimum	-	1	-	-	-	1.70	-	-	-	-	-

Table 2. Summary of phosphorus and nitrate hysteresis trajectories observed in the River Enborne between January 2010 and December 2011.

Storm peak number	Peak date	Days since previous storm peak	Maximum discharge	Total reactive phosphorus		Nitrate-N	
				Trajectory	Loop size	Trajectory	Loop size
			($m^3 s^{-1}$)		($\mu g P l^{-1}$)		($mg N l^{-1}$)
1	17 January 2010		25.1	No data		Anticlockwise	-0.3
2	23 January 2010	6	10.5	Figure 8		Anticlockwise	-0.2
3	29 January 2010	6	7.0	Clockwise	3	Clockwise	0.1
4	05 February 2010	7	3.0	Anticlockwise	-8	Clockwise	0.2
5	16 February 2010	11	4.5	Clockwise	6	No hysteresis	
6	19 February 2010	3	3.2	Clockwise	25	Clockwise	0.6
7	22 February 2010	3	7.5	No hysteresis	0	Clockwise	0.2
8	28 February 2010	6	12.6	Clockwise	15	No hysteresis	
9	20 March 2010	20	2.8	No hysteresis		Clockwise	0.9
10	26 March 2010	6	7.7	Clockwise	25	Figure 8	
11	30 March 2010	4	5.5	Clockwise	60	Clockwise	0.2
12	03 April 2010	4	8.0	Clockwise	30	No hysteresis	
13	02 May 2010	29	1.5	Anticlockwise	-70	Clockwise	0.8
14	17 May 2010	15	1.5	Anticlockwise	-200	Clockwise	0.8
15	23 August 2010	98	1.4	Clockwise	160	Clockwise	1.4
16	26 August 2010	3	2.5	Clockwise	130	Clockwise	0.6
17	24 September 2010	29	5.2	Clockwise	60	Clockwise	1.1
18	02 October 2010	8	2.1	No hysteresis		Clockwise	1.2
19	08 November 2010	37	2.4	Clockwise	66	Clockwise	0.4
20	12 November 2010	4	3.1	Clockwise	23	Clockwise	1.0
21	06 December 2010	24	1.0	Clockwise	100	Clockwise	0.9
22	07 January 2011	9	7.5	Clockwise	116	Anticlockwise	-0.5
23	11 January 2011	4	6.8	Clockwise	118	No hysteresis	
24	18 January 2011	7	10.8	Clockwise	50	Anticlockwise	-0.8
25	11 February 2011	24	3.3	Clockwise	18	Clockwise	0.6
26	14 February 2011	3	5.7	Clockwise	40	No hysteresis	
27	20 February 2011	6	3.2	No hysteresis		Clockwise	0.4
28	28 February 2011	8	3.7	No data		No hysteresis	
29	08 May 2011	69	1.8	Anticlockwise	-24	Clockwise	2.0
30	13 June 2011	36	0.9	Clockwise	50	No hysteresis	
31	18 August 2011	66	2.4	No data		Figure 8	
32	27 August 2011	9	1.6	Clockwise	65	Clockwise	1.4
33	04 November 2011	69	1.8	Clockwise	35	Anticlockwise	-1.3
34	13 December 2011	39	12.1	No data		Anticlockwise	-2.1
35	16 December 2011	3	2.9	No data		Clockwise	0.3
36	24 December 2011	8	2.1	No data		Clockwise	0.5

Figure 1. Map of River Enborne catchment.

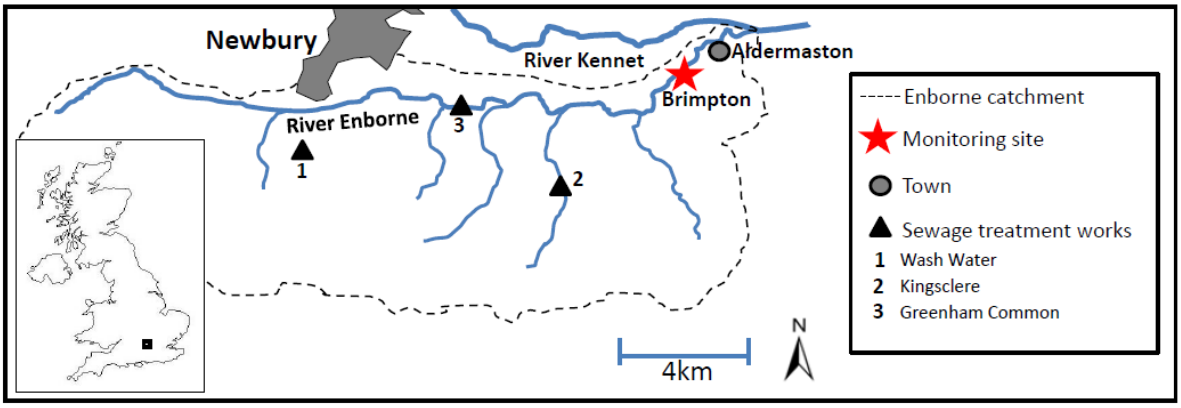


Figure 2. High-frequency monitoring data for the River Enborne at Brimpton: (a) Total reactive phosphorus hourly data, with TRP and SRP manual ground-truthing data; (b) Nitrate hourly data, with weekly manual ground-truthing data; (c) Rainfall data (from CEH Wallingford meteorological station); and (d) River flow at Brimpton, with each storm event numbered consecutively (supplied by the Environment Agency and CEH National River Flow Archive).

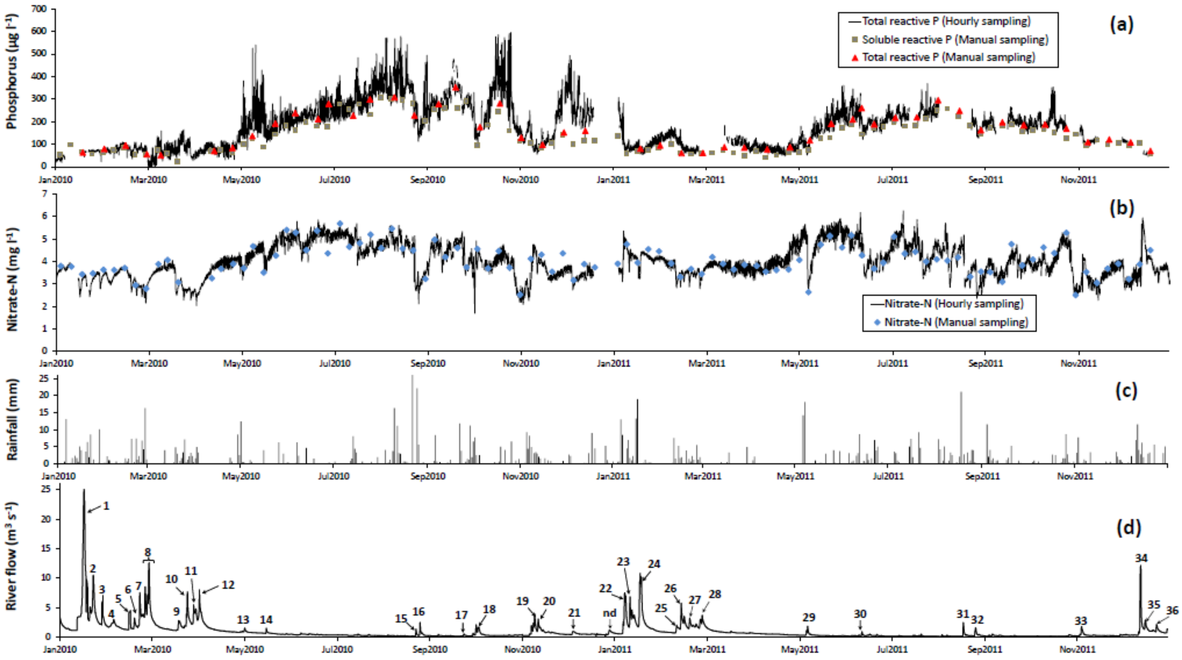


Figure 3. Nutrient concentration-flow relationships in the River Enborne from January 2010 to December 2011. Major hysteresis loops identified by their associated storm event numbers (Figure 2d).

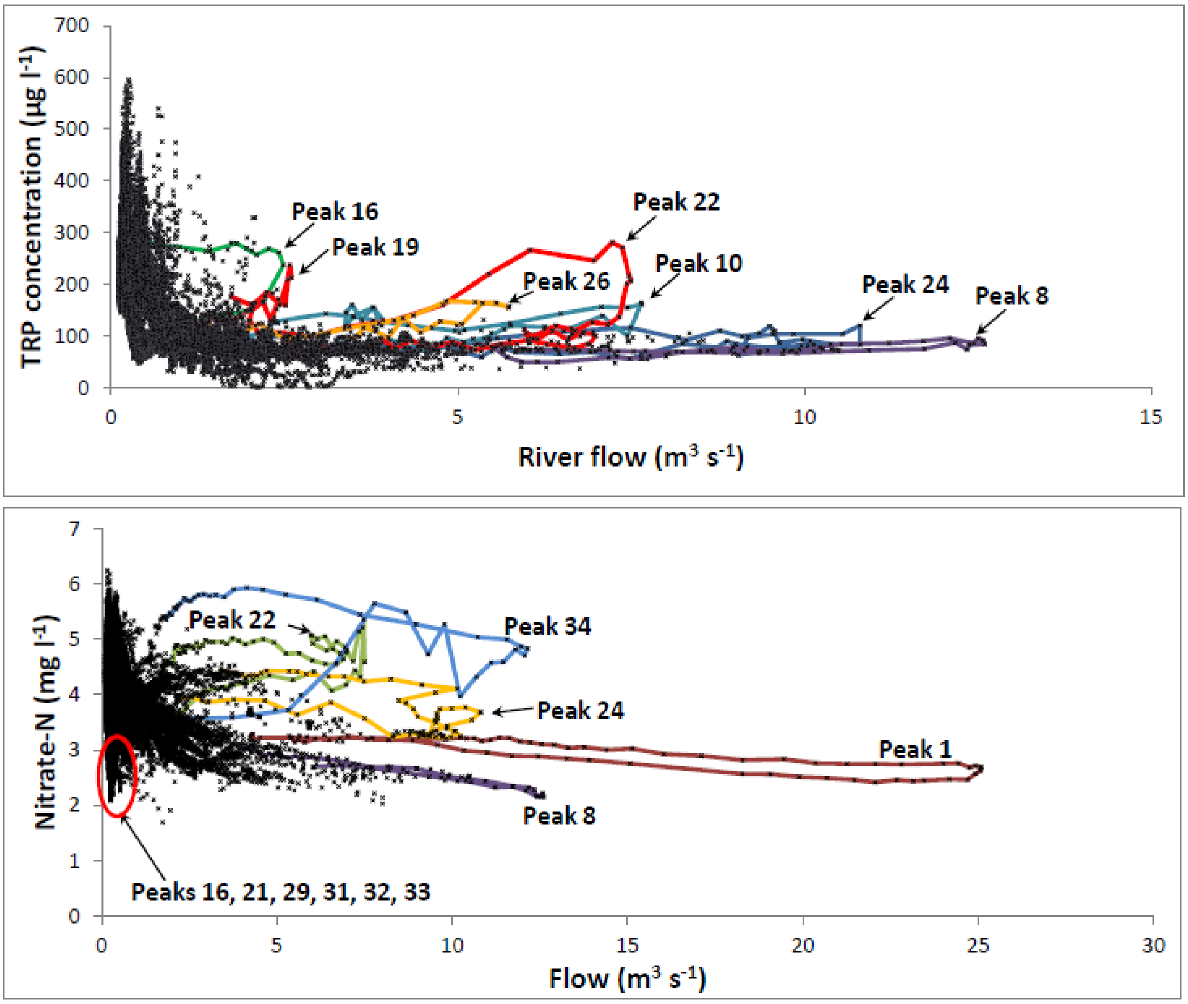


Figure 4. Total reactive phosphorus (**x**) and nitrate (□) concentration-flow relationships at monthly resolution throughout the two year monitoring period.

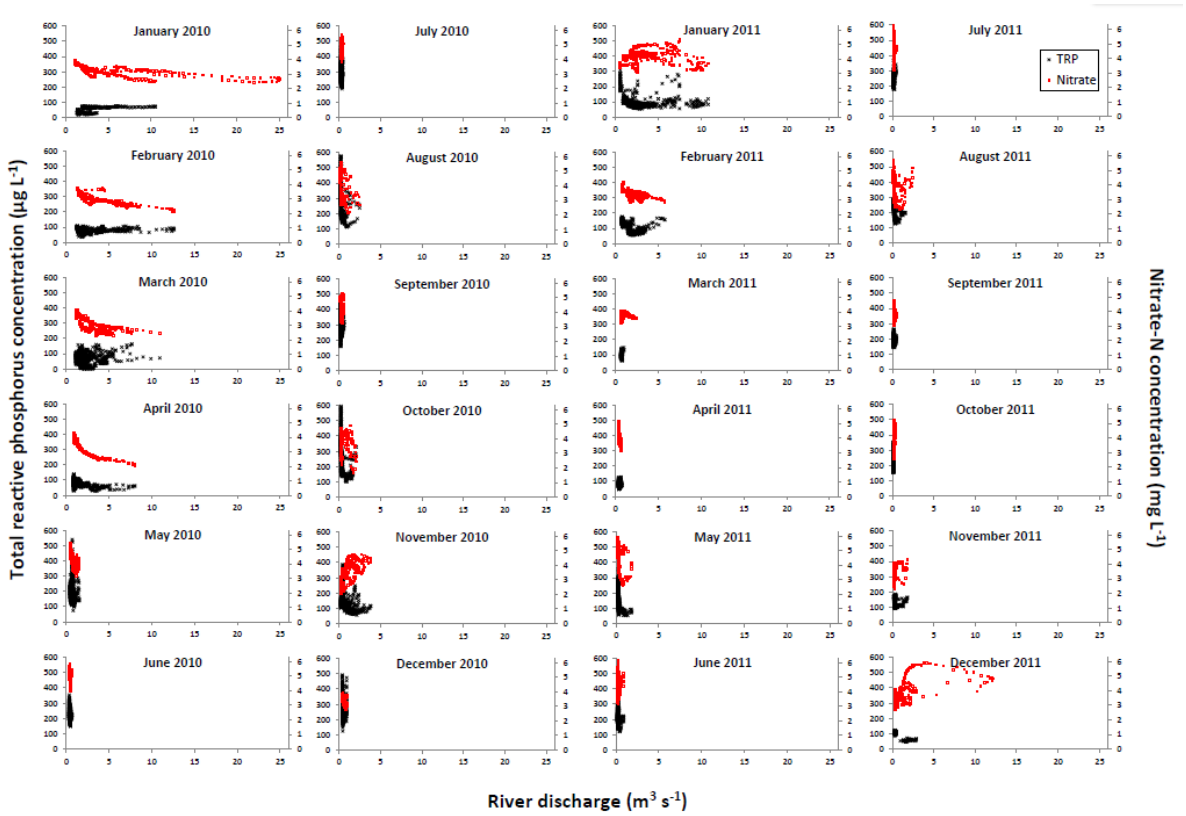


Figure 5. Total reactive phosphorus and nitrate-N hysteresis trajectories throughout the two-year monitoring period (nd = no data).

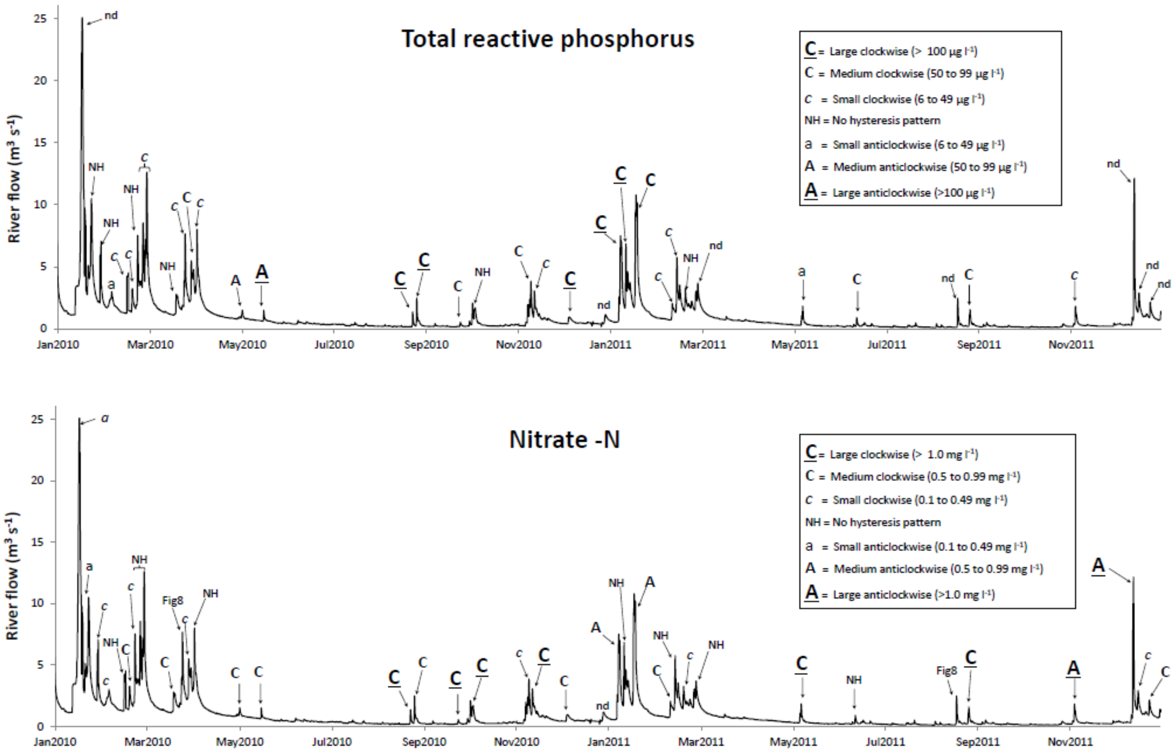
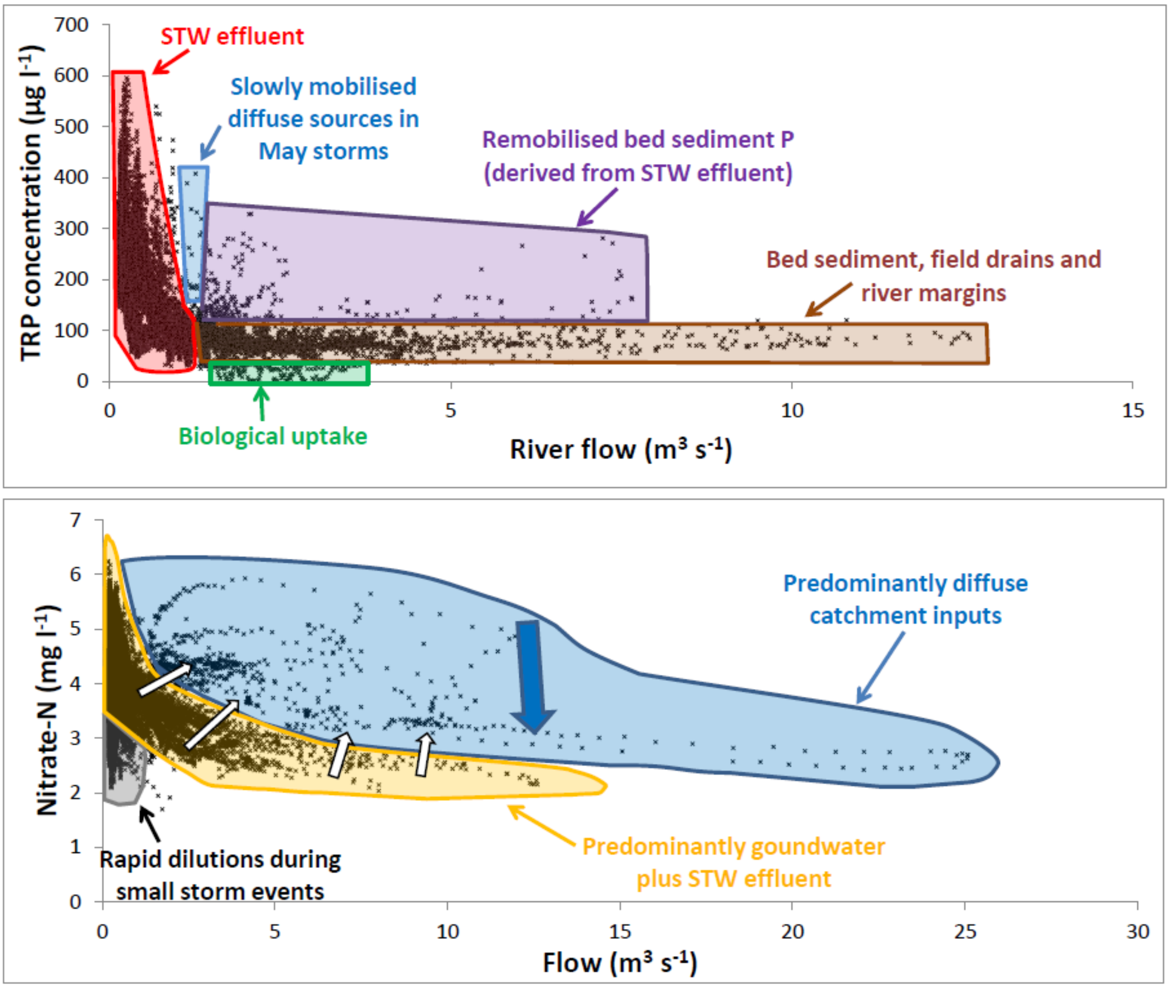


Figure 6. Summary of the predominant total reactive phosphorus and nitrate sources to the River Enborne, determined by a combined investigation of the time series, concentration-flow relationships and nutrient hysteresis patterns during storm events. Filled arrows indicate depletion of slowly-mobilised diffuse nitrate sources through the series of winter storms. The unfilled arrows indicate increases in the proportion of rapidly-mobilised rain-related nitrate inputs to the river.



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